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(54) Ultra-thin self-assembling molecular films and apparatus and method for making them and applying them to surfaces.

(57) An ultra-thin, self-assembling molecular film has ordered amphiphilic molecules that are oriented relative to one another in two directions.

The film is made by delivering a substantially continuous curtain of film-forming solution containing amphiphilic molecules to a surface of an aqueous liquid, confining the film-forming solution against movement in all but one direction along the said surface, whereby the film-forming solution solidifies into a self-assembling molecular fluid membrane in which the molecules are ordered and arranged in aligned units that are themselves oriented relative to one another in two directions generally parallel to the said surface.

Apparatus for carrying out this method comprises liquid-holding means (A) for holding an aqueous liquid having a liquid surface and on which a film-forming solution containing amphiphilic molecules is solidifiable, the said liquid-holding means (A) having side boundaries (14, 16) at opposite ends of a width dimension extending substantially perpendicular to a film-forming direction, and delivery means (B) for delivering a film-forming solution containing amphiphilic molecules to the liquid-holding means (A) in a substantially continuous thin stream extending substantially continuously across the said width dimension, whereby the solution floats in an aqueous liquid held by the liquid-holding means (A) and solidifies into the desired film.

The film may be applied directly to a substrate as it is produced.

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ULTRA-THIN SELF-ASSEMBLING MOLECULAR FILMS AND APPARATUS AND METHOD FOR MAKING THEM AND APPLYING THEM TO SURFACES

This application relates to ultra-thin films, and to apparatus and methods for making such films. The invention is more particularly but not exclusively applicable to self-assembling molecular films and will be described with particular reference thereto. However, it will be appreciated that the invention has broader aspects and can be used for making other types of films, such as polymer thin films.

Known techniques for making thin films, such as the conventional Langmuir-Blodgett technique, Katharine B. Blodgett, J. Am. Chem. Soc.; (1935), 57, 1007-1022, involve dropping a solution of film-forming substrate and solvent on the surface of water, and letting the solvent evaporate. This leaves behind the amphiphilic molecules to self-assemble on the surface of water to form a film, which is then compressed to align the molecules in the film. This film has certain fixed domains and cannot be manufactured in a continuous, unbroken state.

Another technique disclosed in U.S. Patent Specification US-A-4,765,939 involves dropping a solution of film-forming polymer and solvent on the surface of water, and allowing the solvent to evaporate to air. This leaves behind a thin film membrane of the polymer formed on the surface of the water. All these previous techniques for making thin films or membranes containing amphiphilic molecules or polymers are such that the molecules are arranged in random disorientation.

As used in this specification, the term "self-assembling molecular film" means one in which the molecules self-assemble into an ordered film.

An ultra-thin self-assembling molecular film has ordered amphiphilic molecules that are oriented relative to one another in two directions. A film of this type is formed by confining the film during its formation in such a manner that the molecules are ordered in two directions, and are not allowed to become randomly disoriented, as they do in known techniques.

The present invention provides a film made from a film-forming solution containing amphiphilic molecules in which the molecules are ordered in the film and are arranged in the film in a plurality of aligned units, and the aligned units are oriented relative to one another in two directions.

In accordance with the present invention, a self-assembling molecular fluid membrane is prepared by delivering a substantially continuous curtain of film-forming solution containing amphiphilic molecules to a surface of an aqueous liquid, confining the film-forming solution against movement in all but one direction along the said surface, whereby the film-forming solution solidifies into a self-assembling molecular fluid membrane in which the molecules are ordered and arranged in aligned units that are themselves oriented relative to one another in two directions generally parallel to the said surface.

Also in accordance with the present invention apparatus for manufacturing film from a film-forming solution containing amphiphilic molecules comprises liquid-holding means for holding an aqueous liquid having a liquid surface and on which a film-forming solution containing amphiphilic molecules is solidifiable, the said liquid-holding means having side boundaries at opposite ends of a width dimension extending substantially perpendicular to a film-forming direction, and delivery means for delivering a film-forming solution containing amphiphilic molecules to the liquid-holding means in a substantially continuous thin stream extending substantially continuously across the said width dimension, whereby the solution floats in an aqueous liquid held by the liquid-holding means and solidifies into a self-assembling molecular thin film with its molecules ordered throughout the film and arranged in a plurality of aligned units that are oriented in a direction substantially perpendicular to the liquid surface and in a direction substantially parallel to the film-forming direction.

In carrying out the method of the present invention, a film-forming solution containing amphiphilic molecules and solvent is delivered to an aqueous or other liquid. The solvent dissolves in the liquid and leaves behind the pure amphiphilic molecules on the surface of the aqueous liquid to solidify into an ultra-thin, self-assembling molecular film. The amphiphilic molecules from the film-forming solution self-assemble in their natural equilibrium condition.

Film made in accordance with the present application can have anywhere from 0 to 100% crystallinity. The percentage of molecules that will crystallise in the film can be controlled by adding chemicals that reduce the crystallising action.

Even though the film has very little actual crystallinity or is completely amorphous, the film still has aligned regions under an optical microscope. The ordered nature of the molecules can be determined by x-ray diffraction, and the orientation of the crystals can be determined by use of an optical microscope. For convenience of description, whether the film is one having actual crystals or simply aligned regions in an amorphous state, the crystals and regions will be referred to as aligned units. Also, reference to an ultra-

thin, self-assembling molecular membrane or film is intended to include an amorphous type of film having aligned units that look like crystals but really are not true crystals.

Film made in accordance with the present application can be applied to glass, ceramic, or porcelain surfaces. The film can also be applied to metal, plastics, and other substrate surfaces to protect and modify such surfaces. For example, polypropylene packaging does not accept many types of ink and film of the present application can be applied to the packaging for printing on the film with these inks. Film of the present application is also a very good anti-corrosion coating for metals.

The film of the present application can be applied to substrates in its ultra-thin, self-assembling molecular membrane or film structure in which each molecule can move up and down perpendicular to the plane of the film but cannot rotate or move in other directions. This helps each molecule to attach and freeze in place on the substrate surface. The polar groups of the film are adsorbed to a substrate surface by forces that include chemical bonding, dipolar attraction, hydrogen bonding and van der Waals forces. The film is then dried in situ on the substrate surface.

Film made in accordance with the present invention can form simultaneous multilayers of individual self-assembling molecular films separated from one another by a thin film of a liquid. The number of layers formed, and the thickness of the film, can be varied by controlling the rate at which additional film-forming solution is delivered and the rate at which solidified film is removed. The film-forming solution can be delivered above or below an aqueous liquid for solidification on the surface of the aqueous liquid. Stacked self-assembling molecular films from different film-forming solutions can be formed to provide a film having layers of different materials. Solidified film is removed from an aqueous liquid by lifting the film at an angle preferably less than 30° in order to minimise the possibility of disrupting the self-assembling molecular nature of the film.

It is also possible to arrange layers of an aqueous liquid and an oil that is immiscible with water, and to solidify film from film-forming solution at the interface of the oil and aqueous liquid layers. It is possible to vary the density of the aqueous solution by adding variable amounts of glycerol or other substances.

The film of the present invention is thus an ultra-thin, self-assembling molecular film that has better properties than previously known films. The apparatus and method of the present invention make such a film in a relatively simple, economical and continuous manner, which was not possible before.

In the accompanying drawings, which illustrate but do not limit the invention:-

Figure 1 is a side elevational view of an apparatus for making film in accordance with the present application;

Figure 2 is a partial top plan view taken generally on line 2-2 of Figure 1;

Figure 3 is a partial cross-sectional elevational view showing amphiphilic molecules solidified on the surface of an aqueous liquid;

Figure 4 is a plan view taken generally on line 4-4 of Figure 3 and showing the ordered state of the molecules as would be determined by x-ray diffraction;

Figure 5 is a view similar to that of Figure 4 and showing the oriented nature of the crystals or aligned units in which the molecules are arranged as would be determined by use of an optical microscope;

Figure 6 is an arrangement showing how the aligned units defined by the crystals or amorphous strips appear in prior art film;

Figure 7 is a partial cross-sectional side elevational view showing film being formed by the simultaneous formation of a plurality of individual layers of self-assembling molecular membranes;

Figure 8 is a side elevational view showing an arrangement for coating small articles with film made in accordance with the present application;

Figure 9 is a partial top plan view taken generally on line 9-9 of Figure 8;

Figure 10 is a side elevational view showing another arrangement for coating small articles with film;

Figure 11 is a side elevational view showing another arrangement for making film;

Figure 12 is a side elevational view showing still another arrangement for making multilayer film by simultaneously forming individual films or layers of different materials;

Figure 13 is a partial side elevational view of another arrangement for delivering film-forming solution to an aqueous liquid; and

Figure 14 is a perspective illustration of another apparatus for forming film and transferring it onto a substrate surface.

Referring now to the drawings, Figure 1 shows a liquid-holding means A that may take many forms, and is illustrated as a generally rectangular trough having end walls 10, 12 and substantially parallel opposite side walls 14, 16.

Liquid-holding means A holds an aqueous liquid 20 that may be distilled water or water having certain other substances dissolved therein. For example, glycerol may be mixed with water to vary the density of

the aqueous liquid. In any case, liquid 20 is of type for which polar groups of amphiphilic molecules have a strong affinity.

Delivery means B for film-forming solution extends substantially completely across liquid-holding means A between its side walls 14 and 16 and closely adjacent to one end 12. Delivery means B includes an elongated outlet or slit 22 extending substantially completely and continuously across the entire width of liquid holding means A between side walls 14 and 16. An elongated porous member 24 can be provided to cover or fill the delivery slit for the film-forming solution. THis provides a diffuser for reducing the velocity and increasing the static pressure of the film-forming solution passing through it. The porous member can be a fabric wick, or can be an open-cell porous material such as air stone or sponge.

When it is stated that outlet or slit 22 and diffuser 24 extend substantially continuously and completely across the entire width of liquid holding means A, it will be recognised that it is possible to provide a plurality of closely spaced slits or holes in delivery means B. Thus, while a plurality of individual streams of film-forming solution would be delivered, they are so closely spaced together across the width of liquid-holding means A that they merge with one another shortly after delivery to provide a substantially continuous curtain of film-forming solution across the entire width of liquid-holding means A.

Delivery means B can simply be an elongated tube with closed ends and having an elongated longitudinally extending outlet slit. Obviously, internal baffles or variations in the cross-sectional area of the passages can be provided for enabling substantially uniform delivery of film-forming solution across the entire width of the delivery means and the liquid-holding means.

Film-forming solution is delivered through a suitable conduit 26 and adjustable valve 28 to delivery means B. This makes it possible to vary the delivery rate of the film-forming solution and to vary the pushing force provided on the solidified film being formed. Obviously, other arrangements, such as a variable speed pump, can also be provided to vary the delivery rate of the film-forming solution.

In the arrangement shown in Figure 1, the outlet 22 and diffuser 24 are located beneath the upper surface of aqueous liquid 20. With this advantageous arrangement, solvent in the film-forming solution dissolves in aqueous liquid 20 instead of flashing off into the atmosphere.

End 10 of liquid-holding means A can be slightly smaller in height than end 12 so that aqueous liquid 20 would continuously flow at a slow rate over end 10. A suitable inlet is then provided for liquid holding means A to continuously supply fresh or reconditioned aqueous liquid 20 to liquid holding means A.

As film-forming solution 30 is delivered into aqueous liquid 20 by delivery means B, it floats to the surface of aqueous liquid 20 and solidifies into a self-assembling molecular film C.

Film pick-up or removal means is provided for removing film C from the surface of aqueous liquid 20. In one arrangement, a roll 34 of plastics or metal foil, wax paper, release grade polyethylene, or polymeric material having a release grade silicone or polyethylene layer on its surface is provided. The roll of material 34 provides a web 36 extending substantially completely across the width of liquid-holding means A between side walls 14 and 16.

Web 36 travels around a roll 38 and then to a take-up roll 40 mounted by adjustable mounting means such as elongated slots 42 in mounting members 44. Adjustment of take-up roll 40 makes it possible to vary the pick-up angle 50 between the upper surface of aqueous liquid 20 and external web portion 36a. Angle 50 is desirably less than 45°, and is preferably less than 30°.

An adjustable angular velocity detector 52 may be connected with roll 38 and with a variable speed drive motor 54 for take-up roll 40 in order to provide movement of web 36 at a substantially constant velocity. Adjustment of angular velocity detector 52 makes it possible to increase or decrease the velocity of the web to vary the rate at which film C is removed from aqueous liquid 20. Solidified self-assembling molecular film C attaches itself to web 36 by molecular attraction and travels with web 36 to take-up roll 40.

As film C solidifies on the surface of aqueous liquid 20, its amphiphilic molecules become frozen because the polar groups attach themselves to the surface of the aqueous liquid. Prior to freezing in place, the molecules are allowed to arrange themselves in their natural equilibrium condition. No external forces are provided which force the molecules to arrange themselves in an unstable condition or beyond their natural equilibrium condition. However, in accordance with the present application, a direction is provided in which the molecules can arrange themselves into aligned units that self-assemble in aligned relationship to one another.

In part, this is made possible by extruding the film-forming solution through a very narrow slit to shear the film-forming solution as it is delivered, and also by delivering the film-forming solution across substantially the entire width of liquid-holding means A between side walls 14 and 16. With the film-forming solution extending in a substantially continuous curtain across the entire width of liquid-holding means A as it is delivered by delivery means B, solidification takes place with the film and film-forming solution transversely confined between side walls 14 and 16.

Figure 3 shows film C having polar groups 60 on amphiphilic molecules attracted to aqueous liquid 20, while non-polar groups 62 extend away from aqueous liquid 20.

Figure 4 shows molecules 70 as being ordered within film C. Thus, molecules 70 self-assemble in their natural equilibrium ordered condition. The molecules are ordered in the sense that they are assembled in a uniform relationship relative to one another as opposed to being randomly distributed in a disordered manner. Molecules are ordered on a micron (micrometre) level, which can be determined by x-ray diffraction.

Molecules 70 arrange themselves into crystals or aligned units 72 in Figure 5. Although many aligned units are not crystals, they appear to be crystals when viewed with an optical microscope. Therefore, whether the molecules are arranged in crystals or only aligned units, both arrangements will be referred to as aligned units 72. Aligned units 72 are oriented relative to one another in both x and y directions, that is, in a direction parallel to film-forming direction x and in direction y transverse or perpendicular to film-forming direction x. By confining the film-forming solution between side walls 14 and 16, aligned units 72 are made to orient themselves relative to one another both longitudinally and transversely of liquid-holding means A. This provides a solidified film having more uniform properties than previously possible.

Figure 6 shows a prior arrangement in which a drop or supply of film-forming solution 80 placed on the surface of an aqueous liquid solidifies into a thin film having units 82 that are completely disoriented and randomly distributed relative to one another.

Figure 7 shows film C as including a plurality of individual layers or membranes 90, 92 and 94. It has been found that film-forming solution 30 delivered by delivery means B simultaneously forms multilayers 90, 92 and 94. It is not completely understood how this takes place, but it seems to be analogous to the bubble-formation phenomenon. It is possible that additional layers form below and/or above an initial layer. In any case, it has been found that a plurality of individual layers forms and these layers are separated from one another by an extremely thin film or bearing layer of aqueous liquid.

The number of layers 90, 92, 94 that are formed, and thereby the thickness of film C, can be varied by varying the delivery rate of film-forming solution 30, and/or by varying the rate at which solidified film C is removed from the aqueous liquid. Obviously, both delivery and removal can be controlled to vary the film thickness and the number of layers or self-assembling molecular membranes that are formed.

The film-forming solution 30 provided by delivery means B provides a pushing force on film C as it solidifies, while the pick-up or removal means provides a pulling force on such film. At least one of such forces is varied to vary the film thickness and the number of simultaneous multilayers that are formed. Each layer 90, 92, 94 is a monomolecular membrane, and such membranes are assembled to form a multi-molecular film C.

The manner in which the thickness of the film can be varied can be demonstrated with the following calculations:

$dz/dt = (c\,q - p\,W\,v\,z) / p\,W\,L$

dz/dt = rate of change in film thickness (cm/sec)

c = concentration of solution (g/ml)

q = flow rate (ml/sec)

W = nanoCOATER width (cm)

v = pick-up velocity (cm/sec)

z = film thickness (cm)

L = distance between extruder and the film pick-up or removal device (cm)

at steady state (dz/dt = O) therefore,

$z = c\,q/p\,W\,v$

or $z = [c\,q] / [p\,W\,v]$

or z = [PUSH] / [PULL]

TYPICAL EXAMPLE

[PUSH]

if c = 0.1 g/ml

if q = 0.083 ml/sec (5 ml/min)

then,

[PUSH] = 0.008 g/sec

or [PUSH] = mass flow rate

[PULL]

if p = 1 g/ml

if W = 36 cm (14 in)

if v = 15 cm/sec (6 in/sec)

then,
[PULL] = 542 g/cm-sec
or [PULL] = mass flow rate per unit thickness
and,

$$\frac{[PUSH]}{[PULL]} = 1.54 \times 10^{-5}\ cm = 154\ nanometers$$

Figures 8 and 9 show a pair of spaced-apart chains 102, 104 extending around sprockets 105-107, at least one pair of which is rotatably driven. Small article holding means in Figure 9 includes clamps 108 that are clamped on chains 104 and have oppositely disposed arcuate supports 110 connected with clamps 108 by telescoping spring loaded connections 112. Spring loaded connections 112 yieldably bias arcuate supports 110 toward one another.

An article 114 is shown as being held between supports 110. As articles 114 travel through film C, a coating of film C attaches to the surfaces of the articles.

Film removal means D is shown as being in the form of a continuous web 120 extending around rollers 121-123, at least one of which is rotatably driven by a variable speed motor 124. Film removed from aqueous liquid 20 by removal means D can simply be discarded if so desired. This arrangement makes it possible to vary the thickness of film C and thereby the coating thickness applied to articles 114.

Drying means 130 may be provided above articles 114 after they have been coated by film C. Obviously, the conveyor chains can be arranged in an elongated path with heating means 130 located remote from liquid holding means A where articles 114 can be removed and inserted.

The small articles that are provided with a film coating can be of many types, such as lenses.

Figure 10 shows another arrangement wherein a layer 140 of a solvent such as octane or hexane or other alkanes that water is positioned on one side of delivery means B and end wall 10. Layer 140 floats on aqueous liquid 20 to provide an interface 142 therewith. The outlet slit for film-forming solution delivery means B and the diffuser 24 are located for delivering film-forming solution 30 within layer 140. The film-forming solution 30 then sinks through layer 140 to interface 142 where it solidifies into thin film C.

The film-forming solution can also be delivered into an aqueous liquid layer depending upon the film-forming substrate used by lowering the diffuser 24 in the water layer. This then will form the thin film at the interface.

The arrangement of Figure 10 has been shown shortened for convenience of illustration and it will be recognized that it could be elongated to have the removal means for removing film at a predetermined rate to vary the thickness thereof. In the arrangement of Figure 10, e.g., the film-forming solution 30 can be comprised of silanes. The arrangement of Figure 10 makes it possible to solidify film in an anerobic environment, and the solvent used in the film-forming solution can be polar or non-polar.

Figure 11 shows another arrangement wherein a layer 20 of aqueous liquid floats on a bottom layer 150 having a density greater than water. For example, layer 150 can be a phenylmethyl polysiloxane. One brand of such material is available as 710 fluid from Dow Corning. This liquid has a density of approximately 1.11 grams per milliliter and is immiscible in water. Film-forming solution delivery means B is positioned with its outlet and diffuser 24 located for deliverying film-forming solution 30 within layer 150. Film-forming solution 30 then rises to interface 152 between layers 20, 150 where film C solidifies with the polar groups 60 of the amphiphilic molecules attracted to layer 20. This is another arrangement that makes it possible to solidify film C in an anaerobic environment.

Figure 12 shows another arrangement wherein a plurality of layers 20 of aqueous liquid are separated from one another by a plurality of layers 150 of a liquid having a density greater than water and being immiscible in water. The densities of the various layers can be adjusted as by adding various amounts of glycerol to the aqueous liquid, and by adding octane or hexane to the other layers. Film-forming solution delivery means B is provided with two different valves 28, 28a for supplying two different types of film-forming solutions through outlet slits and diffusers 24, 24a. This makes it possible to simultaneously form two films C and C′ from one outlet or diffuser 24, and two additional different films Ca and Ca′ from the other delivery diffuser 24a. These different films can be removed in the manner described with reference to Figures 1 and 2, and can be used for coating articles as suggested with reference to Figures 8-10.

Figure 13 shows another arrangement wherein film-forming solution 30 is fed to a transversely elongated reservoir 170 in a delivery means 172 that extends substantially completely across the side walls

of a liquid- holding means adjacent to one end of it. A spillway 174 is provided over which film-forming solution 30 can flow in a substantially continuous curtain 176 to the surface of aqueous liquid 30 for solidification into film C. A fabric member 180 completely covering spillway 174, and extending from reservoir 170 to a location beneath the surface of aqueous liquid 20 defines flow-enhancing means for enhancing the flow of film-forming solution 30 without having any localized disruptions therein. Flow-enhancing means 180 can be a woven fabric such as cotton and can also take other forms. A woven cotton fabric is a particularly good flow-enhancing means.

Figure 14 shows another arrangement wherein liquid-holding means A′ is divided into two compartments as by a divider 200. One compartment 202 holds an aqueous liquid while the other compartment 204 holds a film-forming solution. Rotatable roller 206 is mounted for engaging an aqueous liquid within compartment 202. Roller 208 is rotatably mounted for engaging film-forming solution within compartment 204. Roller 210 is rotatably mounted between rollers 206, 208 and in an engagement therewith. Roller 210 is suitably rotatably driven as by a variable speed motor 212. Rollers 206-210 may be drivingly connected with one another as by belts 214, 216 extending around pulleys on the ends of the rollers, or they may be driven by engagement with one another.

Belts 214, 216 are preferably twisted to impart rotation of rollers 206, 208 in a direction reverse to that of roller 210. Clockwise rotation of roller 210 results in counterclockwise rotation of 206 which transfers an aqueous liquid from compartment 202 onto the surface of roller 210. Thus, roller 210 and its outer surface becomes a movable liquid holding means for holding an aqueous liquid on which film-forming solution may solidify.

As roller 210 continues to rotate with a thin film of aqueous liquid on the outer surface thereof, roller 208 rotates in a counterclockwise direction and transfers film-forming solution from compartment 204 onto the layer of aqueous liquid on roller 210. As the film-forming solution solidifies on roller 210, it engages the surface of a substrate 220 moving longitudinally past roller 210 as indicated by arrow 222. The polar groups of the self-assembling molecular film attach themselves to the surface of substrate 220 for providing a coating thereon. Substrate 220 may be a web for storing the film or may be an article to be coated with the film. Rollers 206, 208 can be independently driven by individual variable speed motors.

In the arrangement of Figure 14, the pulleys are preferably arranged such that roller 208 is rotating at a greater velocity than roller 210. This provides longitudinal shearing action on the film-forming solution as it is being delivered from roller 208 to roller 210, and this helps to provide ordering of the molecules and orientation of the aligned units. Instead of wetting the outer surface of roller 210 with a roller 206, it is obvious that it is possible to spray an aqueous liquid against roller 210 or to provide a porous surface on roller 210 with an aqueous liquid being supplied internally to roller 210. It is also obvious that a doctor blade or the like can be provided for obtaining a uniform film of aqueous liquid on the outer surface of roller 210.

The film-forming apparatus shown in Figure 14 can be duplicated on the opposite side of substrate 220 for providing a self-assembling molecular film on both opposite surfaces thereof simultaneously.

Film-forming solutions used in accordance with the present application can be made by dissolving an amphiphilic material or "amphiphile," having low solubility and volatility, into a low-boiling organic solvent, such as chloroform, hexane, methylene chloride or the like, or into a polar solvent, such as ethanol, acetone, propylene carbonate or the like.

Materials that can be used to form film in accordance with the present application include, but are not necessarily limited to, the following:

Amphiphilic Acids

Those amphiphiles which include carboxylic acid (-COOH) groups, or their associated salts, as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic acid, elaidic acid, stearic acid, arachic acid, and other naturally occurring fatty acids, as well as synthetic compounds which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions. (A balance must be achieved, as is well known to those skilled in the art, between the length of the alkane or aromatic apolar residues, and the acid residue, in order to provide true monolayer-forming character on a water surface.)

Amphiphilic Alcohols

Those amphiphiles which include alcohol (-OH) groups as the major polar component. The apolar

component typically consists of a long linear alkane segment. Examples include brassidic alcohol, elaidic alcohol, stearic alcohol, arachic alcohol, and other fatty alcohols, as well as synthetic alcohol compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Amides

Those amphiphiles which include amide (-NHCO) groups as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic amide, elaidic amide, stearic amide, arachic amide, and other fatty amides, as well as synthetic amide compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Amines

Those amphiphiles which include primary ($-NH_2$), secondary (-NHR), or tertiary amine ($-NR_2$) groups as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic amine, elaidic amine, stearic amine, arachic amine, and other fatty amines, as well as synthetic amine compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Cyanides

Those amphiphiles which include cyanide (-CN) groups as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic cyanide, elaidic cyanide, stearic cyanide, arachic cyanide, and other fatty cyanides, as well as synthetic cyanide compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Nitrates

Those amphiphiles which include nitrate ($-NO_2$) groups as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic nitrate, elaidic nitrate, stearic nitrate, arachic nitrate, and other fatty nitrates, as well as synthetic nitrate compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Phosphates

Those amphiphiles which include phosphate ($-PO_4$) groups as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic phosphate, elaidic phosphate, stearic phosphate, arachic phosphate, and other fatty phosphates, as well as synthetic phosphate compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Sulphonates

Those amphiphiles which include sulphonate ($-SO_3$) groups as the major polar component. The apolar component typically consists of a long linear alkane segment. Examples include brassidic sulphonate, elaidic sulphonate, stearic sulphonate, arachic sulphonate, and other fatty sulphonates, as well as synthetic sulphonic compounds, which include diacetylene, vinyl-unsaturated, or fused linear or branched aromatic residues within the apolar regions.

Amphiphilic Silanes

Those amphiphiles which include silanol $Si-(X)_n$. Where X = halogens, hydroxy, alkoxy, amine or imine or similar groups as the major polar component, and n = 1-3. The apolar component typically consists of a long linear alkane segment. Examples include brassidic silane, elaidic silane, stearic silane, arachic silane, and other fatty silanes with alkyl chain C_1-C_{16}, as well as synthetic silane compounds, which include diacetylene, vinyl unsaturated, or fused linear or branched aromatic residues within the apolar regions. Silanes can be used to form film in an anaerobic environment, and the solvent used can be either polar or non-polar. The use of non-polar solvents was not heretofore possible.

In addition, amphiphiles having, in their apolar regions, residues or structures comprising organic dyes with and without metal substituents (e.g., phthalocyanines, porphyrins, phenol blues, etc.), inorganic dyes (e.g., chromates, iron oxides, etc.), nonlinear oscillators (e.g., p-nitroanaline and derivates, etc.), and/or photoconductors (e.g., carbazoles, acridones, etc.) are also useful in accordance with the invention.

The general criteria for all of the amphiphiles useful in accordance with the invention is that they should be capable of forming a true self-assembling molecular layer on a water surface (water/gas or water/oil interface), when spread from a solvent. Finally, the amphiphiles useful in accordance with the invention must be virtually insoluble in aqueous media, at certain pHs, with/without certain salt types or concentrations added to the aqueous media. Nearly all commercial polymers can be used to form film in accordance with the present application including, but not limited to, polyesters, polycarbonates, polyamides and fluorocarbons. Materials that form self-assembling molecular multilayers are particularly advantageous to form film in accordance with the present application.

In contrast with known techniques for forming monolayer-like membranes by utilizing very dilute solutions of monomolecular layer-forming materials in a low-boiling solvent, it is preferred in the present invention to use a concentrated solution of such materials, such as the foregoing preferred amphiphilic compounds, in such a solvent. Preferably, concentrations of about 0.01 mg/ml to about 1000 mg/ml are utilized. Optimally, solutions of a concentration of about 0.5 mg/ml to about 20 mg/ml are used. Film-forming solutions are made by dissolving a suitable amphiphile in a suitable low-boiling organic solvent. Usable solvents include, but are not limited to, chloroform, hexane and methylene chloride, and polar solvents such as ethanol, acetone and propylene carbonate.

In previous arrangements, the monolayer formed from the film-forming solution was compressed in order to compress the molecules together in the plane of the film. In contrast, the present application allows the molecules to assemble in their natural equilibrium state. In accordance with the present application, the solvent in the film-forming solution preferably dissolves into an aqueous liquid instead of flashing off into the atmosphere. In addition, the ratio of the delivery rate of film-forming solution to the pick-up rate of solidified film is directly proportional to the film thickness and the number of layers in the film. It is desirable that the delivery means for the film-forming solution provides a pressure drop across the delivery slit that is very low, from 0 to 5 psi. (0 to 35 kPa).

When the film-forming solution contacts the aqueous liquid, an initial film forms and extends across the confined surface area of the trough aqueous liquid. As additional film-forming material is delivered and contacts the aqueous liquid, the film thickens until the desired multi-molecular film thickness is reached. The newly delivered film-forming solution continues to thicken the film by climbing on top of or underneath the trailing edge of the previous monomolecular layer. The amphiphilic molecules simultaneously orient themselves in the z dimension of Figure 1 perpendicular to the surface of the aqueous liquid. The simultaneous volatization or dissolution of the solvent from the amphiphile film-forming solution completes the formation of the film in which the molecules are ordered and also arranged in aligned units that are oriented in the x and y directions of Figure 2.

The use of film-forming solutions that form bubbles are particularly advantageous for making films in accordance with the present application. Film in accordance with the application comprises a plurality of aligned units arranged side-by-side and end-to-end. 100x examination using an optical microscope can be used to distinguish the ordered and oriented film of the present application from a single crystal in a prior art-type of film.

Film made in accordance with the present application can be made in many different thicknesses, but is preferably less than about 6 microns thick. Film of the present application is also characterized by its uniform thickness throughout its area made possible by the monomolecular layers of uniform thickness being intimately attached to one another at their interfaces in a multilayer film.

Claims

1. A film made from a film-forming solution containing amphiphilic molecules in which the molecules are ordered in the film and are arranged in the film in a plurality of aligned units, and the aligned units are oriented relative to one another in two directions.

2. A film as claimed in claim 1 in which the film comprises a plurality of monomolecular layers that include layers made from difference types of film-forming solutions.

3. A film as claimed in claim 1 in which the film-forming solution comprises an ultra-thin, self-assembling molecular material.

4. A film as claimed in claim 1, 2 or 3 having a substantially uniform thickness of less than 6 micrometres.

5. A substrate having a surface coated with a film as claimed in any one of claims 1 to 4.

6. Apparatus for manufacturing film from a film-forming solution containing amphiphilic molecules comprises

liquid-holding means (A) for holding an aqueous liquid having a liquid surface and on which a film-forming solution containing amphiphilic molecules is solidifiable, the said liquid-holding means (A) having side boundaries (14, 16) at opposite ends of a width dimension extending substantially perpendicular to a film-forming direction, and

delivery means (B) for delivering a film-forming solution containing amphiphilic molecules to the liquid-holding means (A) in a substantially continuous thin stream extending substantially continuously across the said width dimension, whereby the solution floats in an aqueous liquid held by the liquid-holding means (A) and solidifies into a self-assembling molecular thin film (C) with its molecules ordered throughout the film and arranged in a plurality of aligned units that are oriented in a direction substantially perpendicular to the liquid surface and in a direction substantially parallel to the film-forming direction.

7. Apparatus as claimed in claim 6 including film-removal means (34, 36, 38, 40) for removing solidified film (C) from the liquid-holding means, in which film-forming solution delivered to the liquid-holding means (A) is acted upon by a pulling force provided by the film-removal means and by a pushing force provided by additional film-forming solution being delivered by the delivery means (B), and control means for controlling at least one of said forces.

8. Apparatus as claimed in claim 6 or 7 including shearing means for shearing said film-forming solution as it is delivered to the liquid-holding means (A).

9. Apparatus as claimed in claim 6, 7 or 8 in which the liquid-holding means comprises a movable roller (206, 208, 210) having an outer roller surface for holding a coating of aqueous liquid in which a film-forming solution containing amphiphilic molecules is solidifiable.

10. Apparatus as claimed in claims 6 to 9 in which the delivery means (B) includes a wick or other porous member extending substantially across the said width dimension and through which the film-forming solution flows to the liquid-holding means (A).

11. Apparatus as claimed in any one of claims 6 to 9 in which the delivery means (B) includes an elongated edge extending substantially across the said width dimension and over which the film-forming solution flows to the liquid-holding means (A), and flow-enhancing means (180) over which the film-forming solution flows to enhance its flow in a substantially continuous thin stream extending across substantially the entire extent of the said width dimension while minimising localised flow disruptions.

12. Apparatus as claimed in claim 6 including a non-aqueous solution that is immiscible in the aqueous liquid and has an interface with the liquid surface, the delivery means being positioned for delivering the film-forming solution within the non-aqueous solution whereby its film-forming solution solidifies into a self-assembling molecular fluid membrane film at the said interface.

13. A method of forming a self-assembling molecular fluid membrane comprising delivering a substantially continuous curtain of film-forming solution containing amphiphilic molecules to a surface of an aqueous liquid, confining the film-forming solution against movement in all but one direction along the said surface, whereby the film-forming solution solidifies into a self-assembling molecular fluid membrane in which the said molecules are ordered and arranged in aligned units that are themselves oriented relative to one another in two directions generally parallel to the said surface.

14. A method as claimed in claim 13 in which delivery of the said film-forming solution is carried out by feeding it into the aqueous liquid beneath its said surface.

15. A method as claimed in claim 13 or 14 in which the aqueous liquid is continuously moved while the film-forming solution is delivered to it.

16. A method as claimed in claim 15 in which the continuous movement of the aqueous liquid is carried out by placing the aqueous liquid on a moving continuous surface of a movable member and the film-forming solution is longitudinally sheared as it is delivered to the aqueous liquid.

thod as claimed in any one of claims 13 to 16 in which the membrane is removed from the aq1 by lifting the membrane from the surface of the liquid at an included angle with the surface of 5°.

hod as claimed in claim 17 in which the membrane is acted upon by a pushing force provided by additional film-forming solution and is acted upon by a pulling force provided by removal of the from the aqueous liquid, at least one of the said forces being controlled.

thod as claimed in any one of claims 13 to 18 in which a plurality of continuous curtains of filmolution is delivered to the surface of the aqueous liquid, the solutions in each curtain being the sarfferent from one another

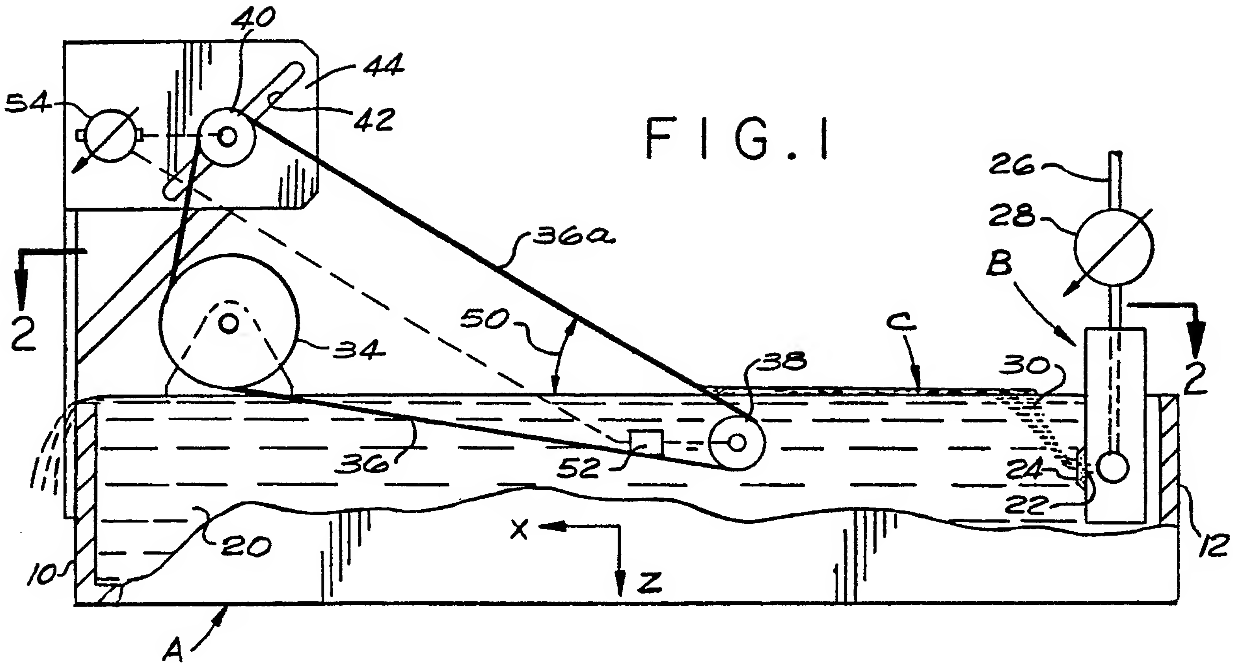


FIG. 1

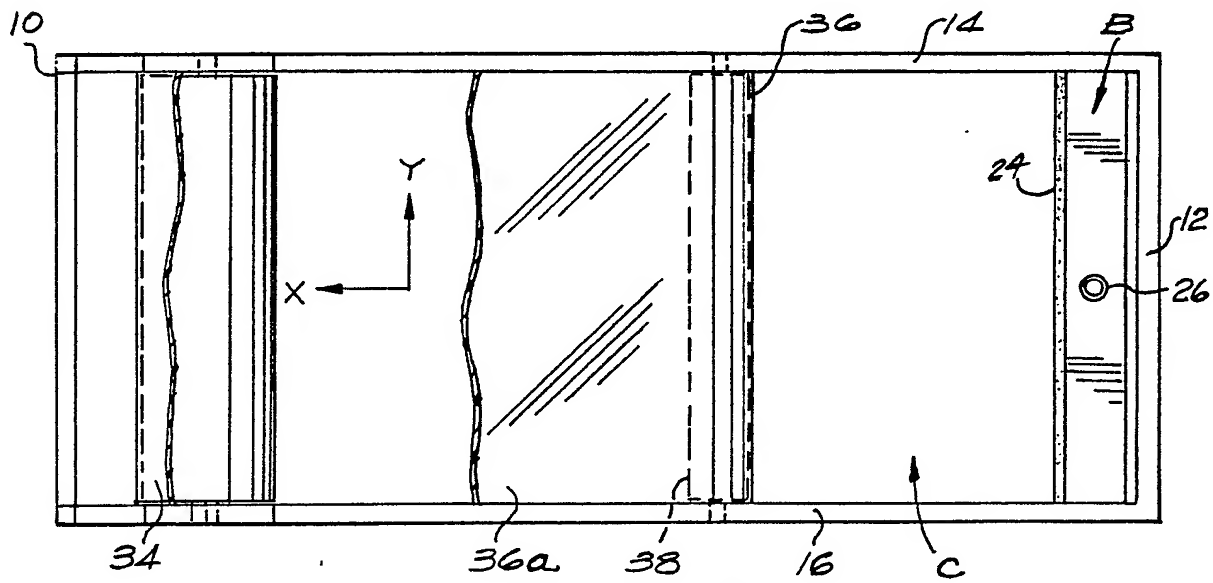


FIG. 2

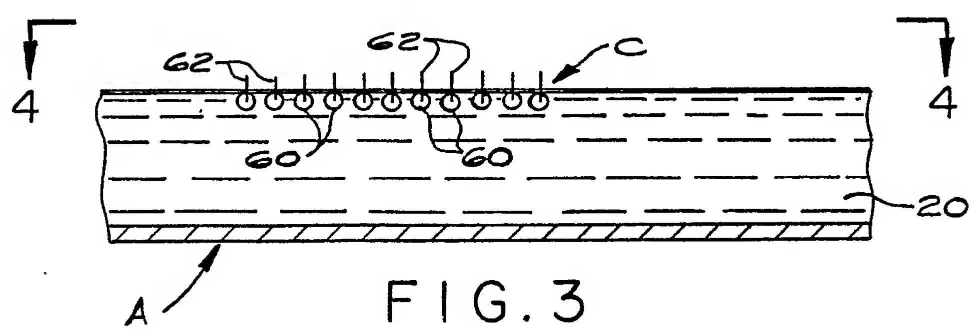


FIG. 3

FIG.4

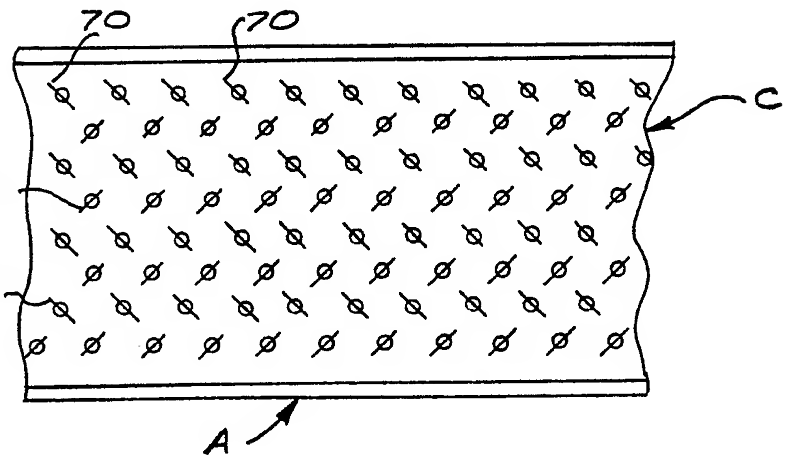


FIG.5

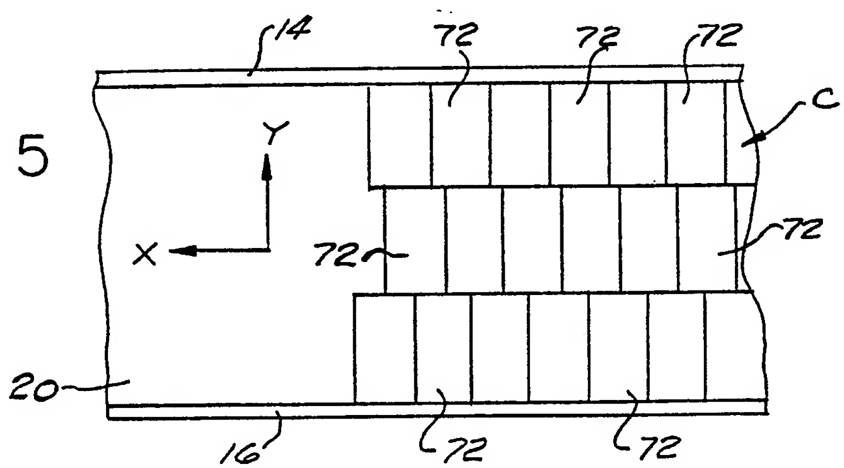


FIG.6
(PRIOR ART)

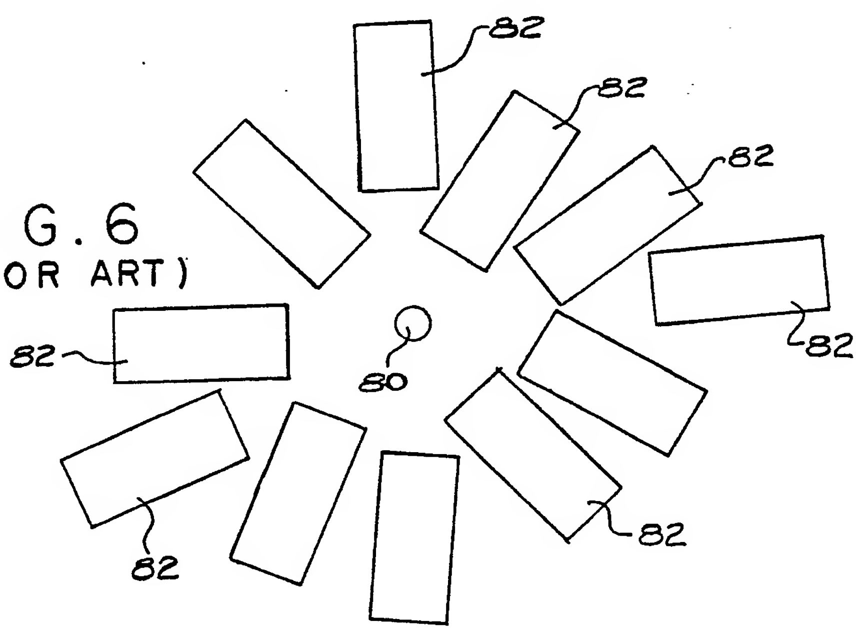
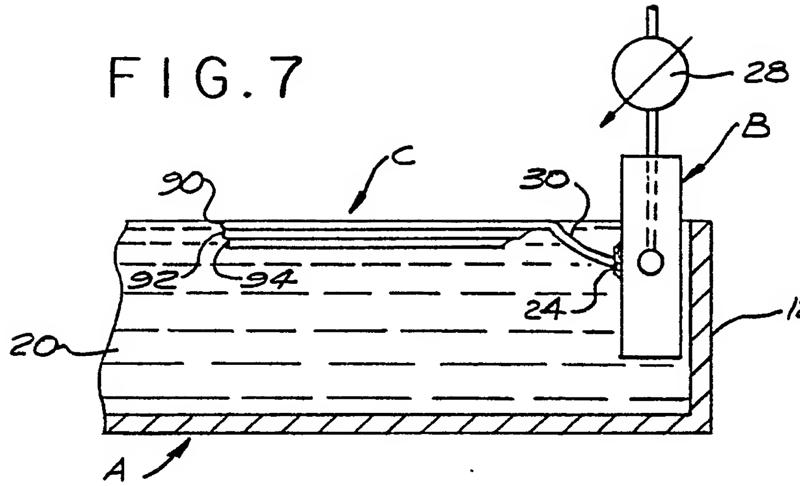


FIG. 7



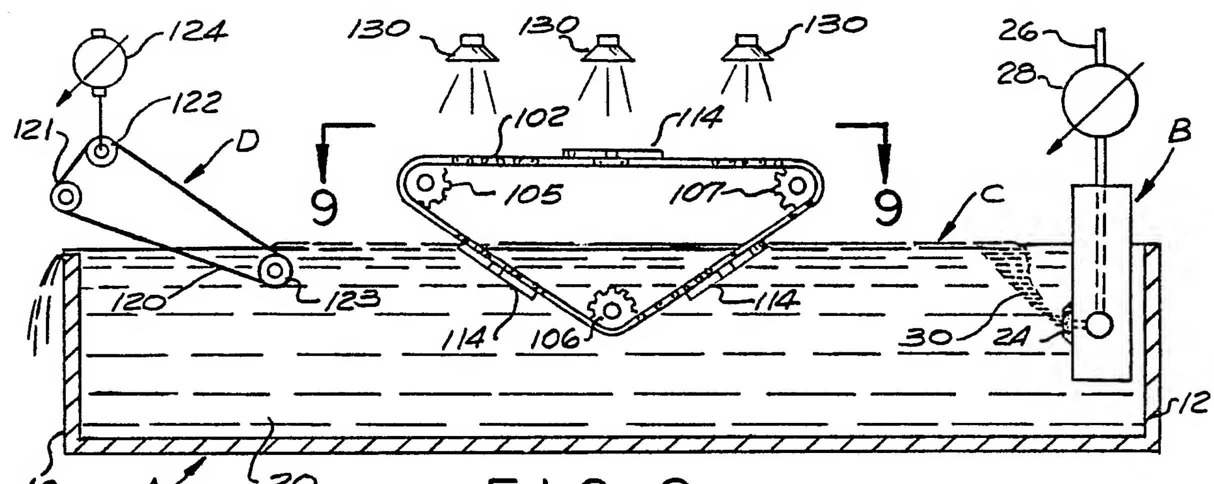


FIG. 8

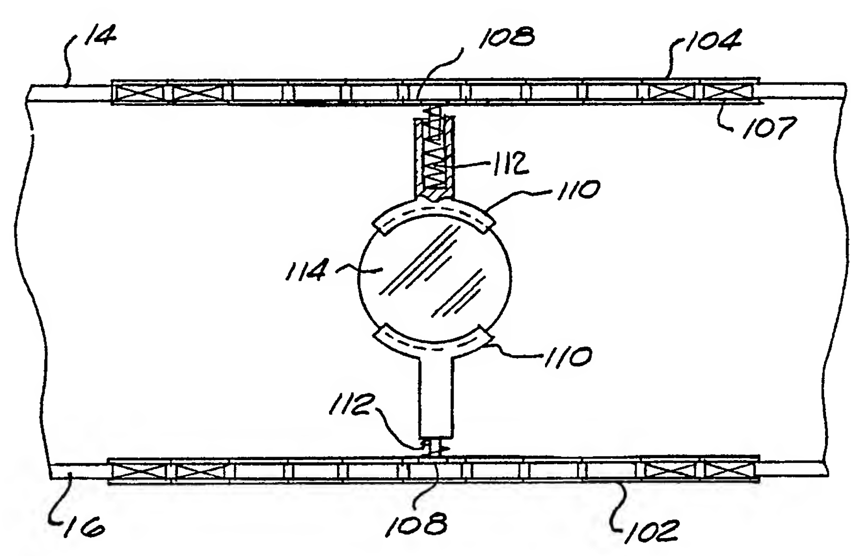


FIG. 9

FIG. 10

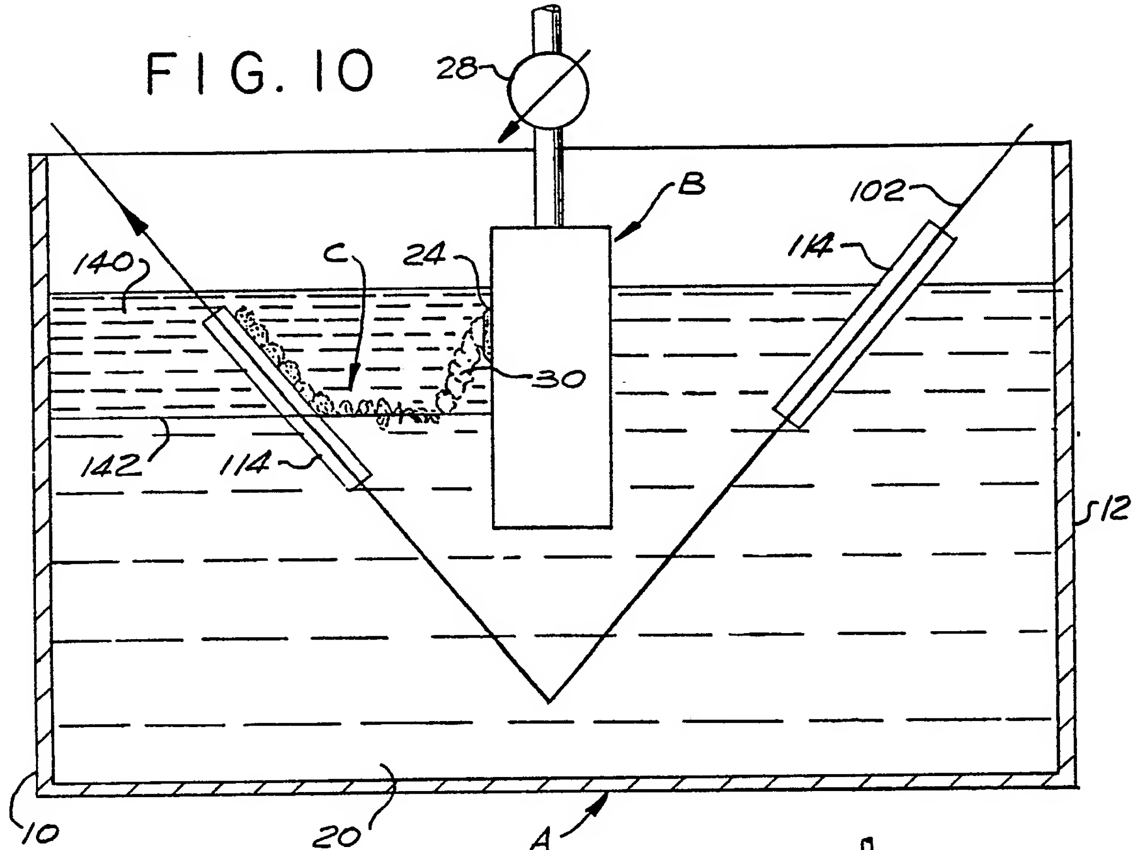


FIG. 11

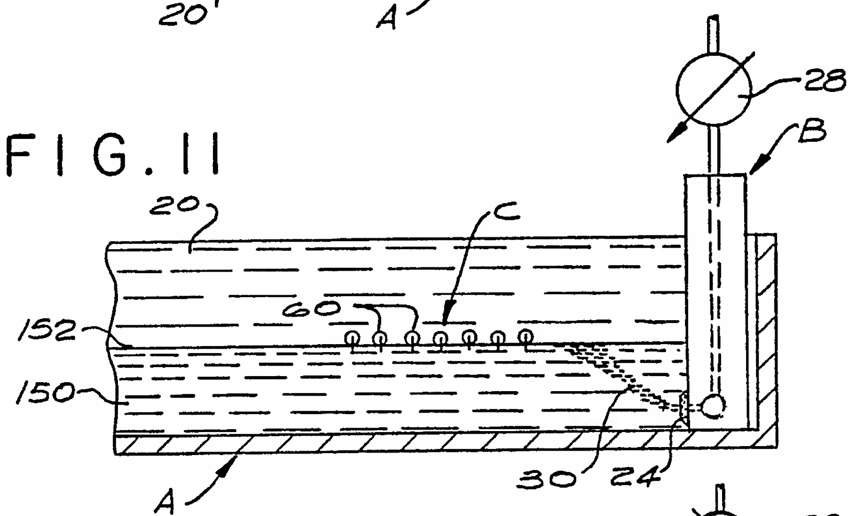


FIG. 12

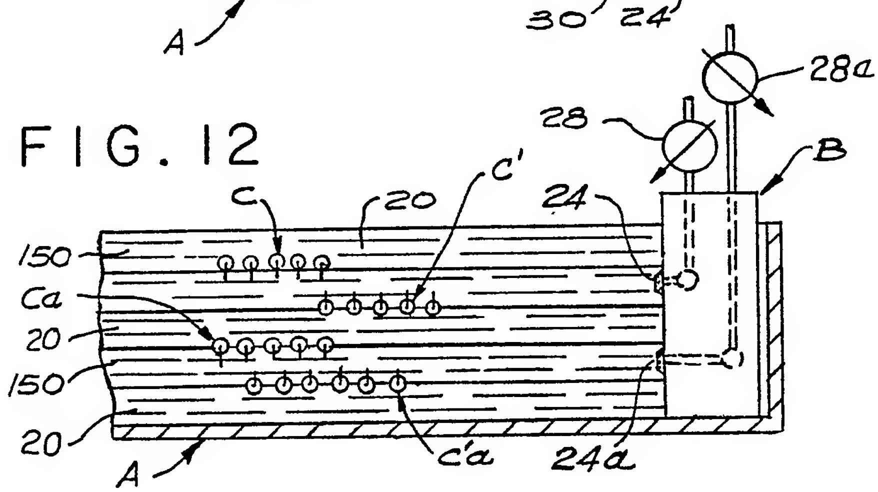


FIG.13

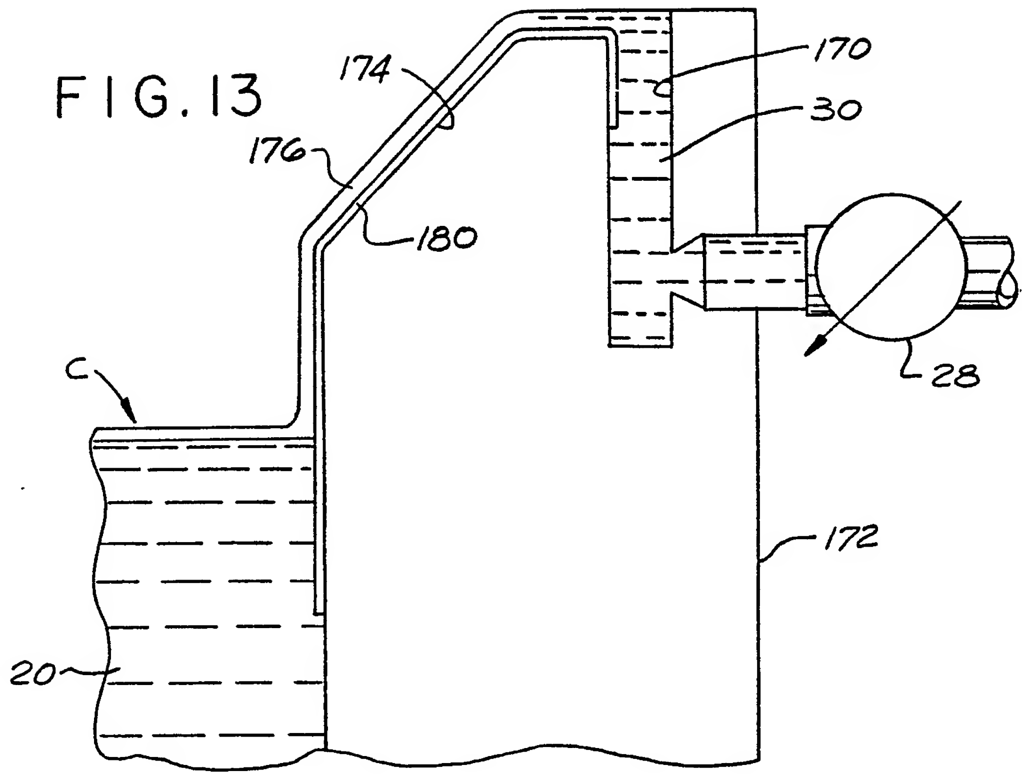

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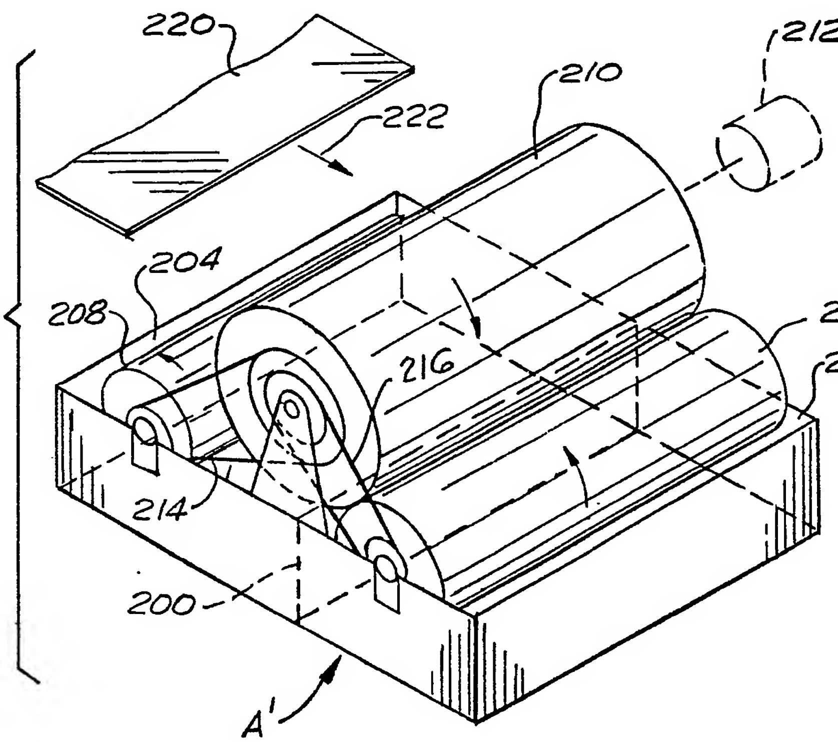
FIG.14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